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Survey of Fouling, Foam, Corrosion, and Scaling Control in Iron and Steel Industry Recycle Systems

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16. ABSTRACT The report gives results of a review of the state-of-the-art for fouling, foaming, corrosion, and scaling control in the treatment and recycle of process waters of integrated iron and steel mills. Areas examined were: (1) the character of the wastewaters generated in the different processes associated with iron and steel making, (2) current treatment practices of the recirculating systems, and (3) corrosion, scaling, fouling, and foaming problems encountered in the treatment processes and current methods for solving them. Much of the iron and steel industry wastewater is derived from noncontact cooling and scrubbing operations. Present technology appears adequate for treatment and control of the noncontact cooling waters. Treatment of the scrubber waters, which are highly contaminated with suspended and dissolved solids and a variety of pollutants, consists of removing the suspended solids and heat loads, decreasing the dissolved solid content by blowdown, and recycling the process water. Chemical scales and deposits constitute a major problem, and are minimized by controlling the chemical stability of the recirculating waters through acid addition and blowdown. Research and development recommended for process water treatment under a high degree of recycle include effective scale inhibition and control, and automatic process water chemical stability monitoring.

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ABSTRACT

The state-of-the art for fouling foaming, corrosion and scaling control in the treatment and recycle of process waters of integrated iron and steel mills was reviewed. Both published literature and on-site data on the following areas collected through visits to process water treatment facilities of selected iron and steel companies were examined: (1) character of the waste waters generated in the different processes associated with iron and steel making, (2) current treatment practices of the recirculating systems and (3) the corrosion, scaling, fouling and foaming problems encountered in the treatment processes and the presently adopted methods for solving them. Possible problems that might be encountered in the application of the present technology to waste treatment in conformity with the 1983 effluent guidelines of the EPA were taken into consideration and recommendations were made for appropriate Research and Development efforts.

The waste waters of iron and steel industry are derived from non-contact cooling and scrubbing operations. Present technology appears adequate for the treatment and control of the non-contact cooling waters. The treatment of the scrubber waters which are highly contaminated with suspended and dissolved solids and a variety of pollutants consists of the removal of the suspended solids and heat loads, decrease the dissolved solid content by blow down and recycle. The formation of chemical scales and deposit constitutes a major problem and this is presently being obviated by controlling the chemical stability of the recirculating waters through acid addition and blow down.

Research and Development efforts recommended for the process water treatment under a high degree of recycle (1983 EPA guidelines) include (a) effective scale inhibition and control (b) automatic monitoring of the chemical stability of the process waters and the corrosion of the materials of construction and (c) sensitive methods for on-line determination and control of phosphate and phosphonate in the recirculating effluents.

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SECTION 1

INTRODUCTION

This report covers the results of a review made on the state-of-the-art for fouling, foaming, corrosion and scaling control in the treatment and recycle of process waters of integrated iron and steel mills. Our approach in this study consisted of (i) determination of the character of the waste waters generated in the different processes connected with the production of iron, steel and steel products in integrated steel mills, (ii) determination of the current practices (methods) for the treatment of the waste waters in recirculating systems, (iii) determination of the problems of corrosion, scaling, fouling and foaming that are encountered in carrying out the treatment of process waters and their recirculation (iv) evaluation of the methods currently being practised by the iron and steel mills for controling these problems (v) extrapolation of the problems under high degree of recycle in accordance with the 1983 effluent guidelines of the EPA, and (vi) a critical review of the problems and the currently-practised methods of control.

The overall objectives of this study are (a) to identify the deficiencies in the current practices, (b) to identify the potential problem areas in extrapolating to the requirements of the 1983 guidelines and (c) to outline the Research & Development efforts that might be undertaken for solving the present and projected future problems.

According to published reports, there are little over 60 integrated steel plants in this country. (An integrated steel mill is one which has both the primary and finishing facilities situated in one location.) It has been generally estimated by a number of reviewers[1,2] that 150-180 cubic meters of water per tonne of raw steel produced are required in the operation of an integrated steel plant. The actual consumption of water might be as little as 5% of the above figure, if appropriate waste treatment and recirculation practices are adopted[2].

Since nearly two thirds of the total flows of water applied in an integrated steel mill are used for the purpose of heat exchange, they remain clean and hence do not require any major treatment. However, the rest of the waters which come into direct contact with the off-gases

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[1]D. Kwasnowski, International Metallurgical Reviews, 20, 137-145 (1975).

[2]R. Nebolsine, Iron and Steel Engineer, 44, 122-135 (1967).

and the products require elaborate treatments prior to being recirculated. In examining the character of the waste waters and their treatment methods, it is important to consider separately the effluent waters (and their associated pollutants) from the different steel making and finishing operations within an integrated steel mill. For this reason, the waste water problem is examined individually for the following major operations (or subcategories):

(1) Coke-ovens
(2) Sinter plant
(3) Blast Furnace
(4) Steel making processes

    (a) Basic oxygen furnace
    (b) Electric furnace
    (c) Open hearth furnace

(5) Hot mills
(6) Pickling
(7) Cold rolling
(8) Metal coating

Section 301 of the Federal Water Pollution Control Act Amendments of 1972 (PL-92-500) requires the achievement of effluent standards of critical parameters for existing industrial point sources (waste waters discharged to navigable waterways) by July 1, 1977 through the application of the "Best practicable control technology currently available" (BPCTCA) and more stringent effluent standards by July 1, 1983 by means of the "Best Available Technology Economically Achievable" (BATEA). The proposed limitation guidelines for the iron and steel industry set by the U.S. Environmental Protection Agency[3] on the basis of BPCTCA and BATEA are summarized in Appendix 1.

The work undertaken toward the realization of the projected objectives may briefly be outlined as follows:

(i) survey of published literature on the subject;

(ii) obtain related documents of EPA;

(iii) visit with steel mills and discuss with the environmental control personnel their methods of waste water treatments;

(iv) visit with the chemical companies that are involved in the treatment of the process waste waters of steel mills and discuss their current methods of treatment, and problems, if any;

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[3] "Development Document for Effluent limitation guidelines and New Source Performance Standards for the Steel Making Segment of the Iron and Steel Manufacturing Point Source Category"; EPA-440/1-74-024-a.

(v) meet with a few design engineers experienced in the design and construction of waste-treatment facilities for the iron and steel industry;

(vi) review the information obtained from (a) published literature (b) steel industry environmental personnel, (c) water treatment companies and (d) design engineers; and

(vii) on the basis of a critical examination of the information gathered and reviewed as indicated above, delineate the current and potential problems of corrosion, scaling, fouling and foaming associated with the waste-water treatments in recirculating systems, and the R&D efforts that might be appropriate.

The visits made to the different steel mills and water treatment companies and the environmental engineers and consultants with whom we met are listed in Appendix 2.

In the following sections of this report, the individual subcategories (processes) of the iron and steel making operations are presented and their waste water treatments discussed.

SECTION 2

CONCLUSIONS

The waste waters from the different sub-categories of the iron and steel making operations consist of non-contact cooling and scrubber waters.

The non-contact cooling waters under closed system operating conditions do not get contaminated except for their corrosion inhibitors and descaling compounds. No major problems of scaling, fouling and corrosion that cannot be handled by applying the available technology have been reported in their treatment and recycle. Systems involving open cooling towers are subject to chemical and biological contamination. Problems of moderate corrosion, scaling and biological fouling associated with these systems are being controlled by the presently available technology.

The scrubber waters are highly contaminated with suspended solids, variety of dissolved solids containing Ca, Mg, Fe, SO_4^{2-}, Cl^-, CO_3^{2-}, and other pollutants such as ammonia, cyanides and a few toxic heavy metals. The current practice for their treatment and recirculation consists of (a) removal of suspended solids. (b) removal of heat loads (c) decrease the dissolved solid content by blow down from the system and (d) recycle them. Formation of chemical scales and deposits and consequent pluggage of the spray nozzles and supply lines appear to be a severe problem of major proportions. A major deficiency rests with the present method of control of scale and corrosion in the scrubber water recirculating systems. This is presently done by controlling the chemical stability of the recirculating waters through the addition of acids and blow down rate. The chemical stability determination is based on calcium carbonate equilibrium and does not take into account (a) the complexing chemical interactions of iron (and other metals) and the anions such as cyanide, ammonia, phenol and other polyanionic organic components and (b) physical, chemical and charge characteristics of the finely divided suspended solids. R&D efforts should be undertaken to develop newer and more effective methods of (1) determining the chemical stability of the recirculating waste waters (2) automatic monitoring of the chemical stability and (3) novel scale control methods.

Systematic data on the chemical and physical characteristics of the process effluents before and after treatment and the nature and amounts of inhibitors for corrosion, scaling and biological fouling are not available in the published literature nor could they be obtained from the waste-water treatment facilities. For an effective technical evaluation of the currently practised waste treatment methods, it is important to know:

(1) chemical analysis of the dissolved and suspended solids of the influent and effluent process waters at different points along the waste treatment,

(2) the chemical nature (structure) of the cationic and anionic polyelectrolytes that are used for the floculations and sedimentation of the finely divided suspended solids in the clarifiers,

(3) the chemical structure of the on-line additives for the control of scaling, corrosion and biological fouling.

Information on (2) and (3) are not available due to their proprietary nature and systematic data on (1) are not readily available.

R&D efforts that are considered necessary for overcoming some of the problem areas identified in this survey and for carrying out an effective treatment and recirculation of the waste-waters, are outlined in the next section.

SECTION 3

RECOMMENDATIONS

On the basis of this review, it is found that a few important problem areas do exist in the treatment and recirculation of the waste waters from the different subcategories of the iron and steel making operations. It is considered that R&D efforts undertaken on the following topics might help alleviate the problems.

EFFECTIVE SCALE INHIBITION

The method currently being practised for the control of scale formation in the recirculating waste-water streams consists of:

(1) determination of the chemical stability of the waste waters by using Ryznar Stability Index (RSI) or Langelier's Saturation Index (LSI),

(2) control of the chemical stability of the system by (a) acid addition and (b) blow down

(3) on-line additions of scale inhibitors and dispersants.

In spite of this treatment, failures in the prevention of CaF_2-type-, and iron compounds-based scales accellerated by the accumulation of finely divided suspended solids are not too uncommon in their occurrance. The present method of control of the chemical stability of the recirculating water system is based on Ryznar Stability Index (RSI) or the Langelier's Saturation Index (LSI) and it does not reflect the complexing interactions of iron and other polyvalent cations and a number of polyvalent anions of inorganic and organic nature. The RSI or the LSI is mainly based on calcium carbonate equilibrium in the environment of the other ions in the system. Further, in the proposed zero discharge recirculating systems, the concentrations of the dissolved solids will be several fold larger than at present and therefore their reactions leading to the formation of scales may be more complex. The scale inhibitor and dispersant systems under these conditions should be able to interact with calcium, iron and any other polyvalent cation in the combined presence of the different anions of inorganic and organic nature. The R&D efforts should consist of:

- an investigation of the chemical and physical characteristics of the process effluents at several points along the recirculating system,

- a critical examination of the chemical stability index and develop modifications to include the complexing interactions discussed above,

- physicochemical studies on the interactions of the effluent cations with a number of selected inhibitor compounds,

- investigation of the physical and chemical characteristics of the finely divided suspended solids and their interactions with the candidate inhibitors, polyelectrolytes and dispersants,

- on the basis of the above, develop inhibitor (and dispersant) systems and conditions for on-line application in an actual water-treatment facility.

AUTOMATIC MONITORING OF THE CHEMICAL STABILITY

Since the chemical stability of the recirculating water system is an important parameter for the control of the conditions of scaling and corrosion in the process waters, continuous monitoring of the chemical stability would be very useful. Hence, instrumentation for its on-line automatic monitoring should be developed. At present, reliable automatic monitoring devices for on-line application are not available. R&D efforts should therefore be undertaken on the following lines:

(1) investigation of one or more physicochemical basis for an effective measurement of this parameter

(2) design and building of the necessary exploratory instrumentation set-up

(3) on-line testing of the operational characteristics of the exploratory model thus developed.

CORROSION AND EROSION MONITORING

Erosion of the metallic surfaces of the materials of construction of the treatment facility by the suspended solids of varying sizes and hardness is an important problem. Further, corrosion of the metallic surfaces underneath the encrustations of chemical scale is another important problem. In order to protect the materials of construction and to prevent any catastrophic failure, appropriate monitoring of erosion and corrosion should be undertaken. Research and development efforts should be undertaken toward the development of automatic corrosion and erosion probes for on-line application. The work will consist of:

1. physicochemical studies and

2. the development of the necessary instrumentation.

DETERMINATION OF PHOSPHATE (PHOSPHONATE) IN THE RECIRCULATING EFFLUENTS

In discussions with one of the chemical companies involved in the treatment of process waters, it was found that for the inhibition of the scale formation and corrosion the inhibitor compounds are added to the recirculating process water system and controlled by a determination of the residual phosphate or phosphonate (from the inhibitor additive) levels. Reliable determination of the residual phosphates at the low levels and in the combined presence of the dissolved and suspended solids in the recirculating waters is a real problem of analytical chemical nature. The lack of proper sensitive determination of phosphate leads to unreliable and somewhat unpredictable control measures in waste treatment. This problem may be magnified several fold under conditions of zero discharge effluent limitation guidelines. Research and development efforts should be directed toward the development of a sensitive analytical method suitable for field application. The development of automatic monitoring instrumentation may be of added advantage.

EXPLORATION OF NOVEL PHYSICAL METHODS FOR CONTINUOUS SCALE REMOVAL

Since chemical scale formation, deposit build up and consequent pluggage of the return lines and scrubber nozzles of the recirculating waste water systems constitute a major problem, it may be worthwhile exploring novel physical methods for their inhibition and control. One such possible approach is the disintegration of "scale and deposit nuclei" build up by the application of magnetic field to the fluid flow system. This principle is currently being practised by a commercial company for domestic water system and biolers. A systematic investigation on the application of this approach might be undertaken.

SECTION 4

PROCESS WATERS, THEIR TREATMENTS AND ASSOCIATED PROBLEMS

COKE OVENS

Coke which is nearly pure carbon is used in the blast furnace (i) as a reducing agent for converting iron ore into iron and (ii) as a fuel. In the United States, the conversion of coal to metallurgical coke is done largely by the by-product recovery process. In this process, bituminous coal is subjected to destructive distillation in the absence of air at 950-1100°C. The volatile matters evolved in this process consist of gases and vapors. The gases include H_2, CH_4, C_2H_6, CO_2, CO, ethylene, butylene, acetylene, H_2S, NH_3, O_2 and N_2. The vaporized liquids in the gaseous mixture consist of ammonia liquor, tar and light oil. The gases, tar and water vapor are taken through the primary coolers. The tar is then separated from the water, which is called the waste ammonia liquor. The direct contact cooling and cleaning of the gases and chemical by-products gives rise to the other major waste waters of the coke-oven plant. Coke dishcarged from the ovens is quenched by water sprays for which generally the source water is directly used. The quenching water is recirculated. Coke is transported to the balst furnace area and the chemicals volatilized during coking process and taken to the by-product plant where ammonium sulfate, tar, pitch and light oil are removed from the coke-oven gas.

The major waste water streams from the coke-oven process thus consist of weak ammonia liquor from primary coolers, final cooler water used for direct contact gas clenaing, benzol-plant waste water derived from stripping operations in benzol recovery plant and cooling water from light oil recovery plants, quench water resulting from the quenching of coke and other wastewaters consisting of tar plant wastes containing phenols, desulfurizer liquor containing thiocyanates and sulfides and pipeline drippings.

Weak ammonia liquor is the waste water for the primary cooler system of coke-oven process amounting to 65 to 150 liters per tonne of coal[4]. The major contaminants in this liquor consist of ammonia, phenol, cyanide, suspended solids and oil. The chemical characteristics of this waste water vary considerably from plant to plant depending upon the coal mix, type of oven, extent and type of by-products recovered and the recovery process

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[4]J. W. Schroeder and A. C. Naso, Iron and Steel Engineer, 1976, p. 60-66.

employed. A typical analysis of the chemical composition of this waste water is presented in Table 1[1]. The varying characteristics of the weak

TABLE 1. TYPICAL ANALYSIS OF WEAK AMMONIA LIQUOR

Component	Concentration mg/l
Ammonia	6900
Cyanide	40
Phenol	870
Thiocyanate	860
Carbon dioxide	440
Total sulphur	1000
Sulphate	35
Hydrogen sulphide	30
Chloride	11000

ammonia liquor from different sources are shown in Table 2.

The final cooling of the coke oven gas utilizes a direct contact water system. Naphthalene is recovered as a by-product from this water. The contaminants of this waste water are: cyanide, phenol, and ammonia. A portion of this water is recirculated to the final coolers and some for coke-quenching.

The waste waters from the plants for the recovery of benzol and light oil are contaminated mainly with oil and small amounts of phenol and cyanide.

Coke-quenching practices differ considerably with the different plants. A number of the plants use the raw water from rivers or lakes for quenching and adopt recirculation system. Some other plants use weak ammonia liquor for quenching.

Tar plant wastes, desulphurizer liquors and gas-line condensate leakages constitute the other miscellaneous waste waters from the coke-oven plants. Phenols, thiocyanates and sulfides are the main contaminants in these waste waters.

The methods of treatment of the coke-oven waste waters essentially consist of (1) removal of ammonia from waste ammonia liquor (WAL) by steam distillation, (2) biological oxidation of the phenolic wastes and other contaminants consisting of cyanides, cyanates and thiocyanates, and (3) sedimentation.

The schematic of a possible multistage treatment of coke-plant waste-waters indicated in the published literature[1] is shown in Figure 1.

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[1] D. Kwasnowski, International Metallurgical Reviews, 20, 137-145 (1975).

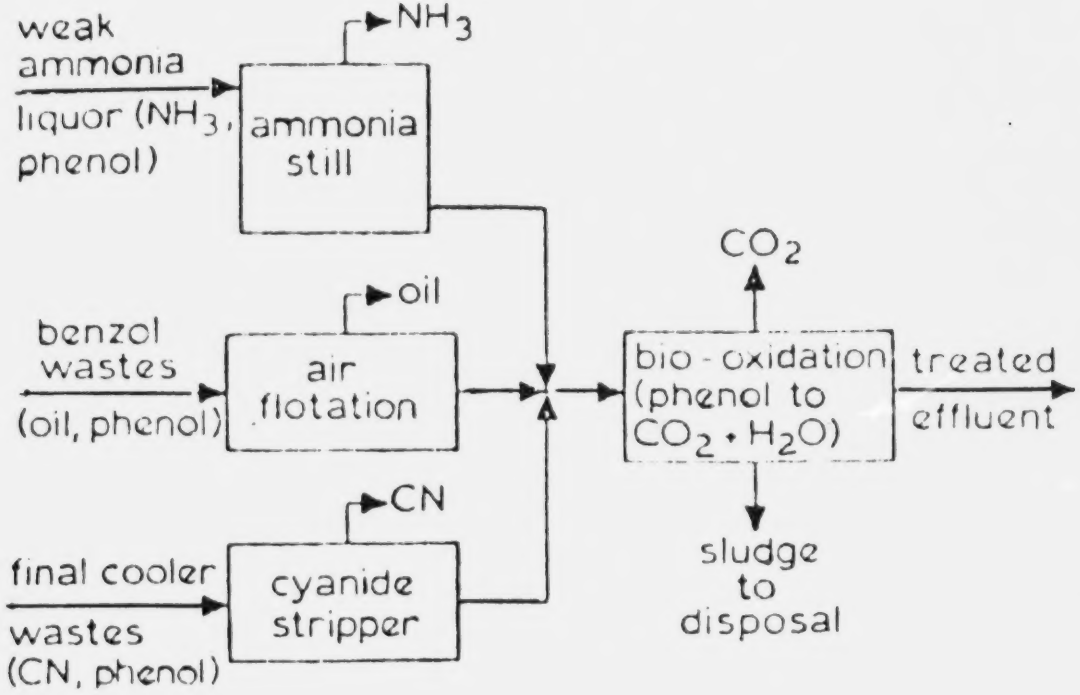

FIGURE 1. TREATMENT OF COKE-PLANT WASTE-WATERS

[TAKEN FROM "WATER POLLUTION CONTROL IN AN INTEGRATED STEEL PLANT", D. KWASANOWSKI, INTL. METALLURG. REV., 20, 137-145 (1975)]

Recirculation is reported only for the final cooler and the coke-quenching waste-water systems. A modular system has recently been developed[4] for the treatment of coke-plant waste waters which utilizes an activated carbon adsorption module for the removal of the organics prior to steam distillation of ammonia. In a parallel operation, the final cooler waters and other waters pass through a clarification unit for the removal of suspended solids and oil, followed by passage through an activated carbon absorption module. A schematic of this is shown in Figure 2.

CORROSION AND SCALING PROBLEMS

Published information on the treatment of coke-oven waste waters do not discuss any major problems of corrosion, scaling and fouling. On the basis of our site visits and telephone contacts with some of the steel companies, it was found that only a few of them carry out the biological treatment in their own facility. After the recovery of the by-products the effluents are generally discharged into minicipal sewers. Further as indicated earlier, only limited recirculation is practiced in the treatment and handling of the final cooler water and quench water. In the event of establishing a recirculating system, there exist the possible problems of chemical scaling (resulting from the lime addition in the steam distillation of ammonia) and corrosion due to the possible pH drops in the recirculating final cooler waters. Systems and conditions can be developed for obviating these problems through the use of caustic soda as a replacement for lime addition and the use of proper pH control.

SINTERING PLANT

In the sintering plant, iron-bearing wastes such as mill scale and finely-divided dust from the basic oxygen furnace, open hearth furnace and blast furnace are blended with fine iron ore and limestone to form an agglomerate that would be suitable for being recharged into the blast furnace. The mixture consisting of the iron-bearing components, limestone and coke fines is placed on travelling grates of the sinter machine and is heated to fusion temperature to produce the sinter. The sintering operation also produces carbon dioxide, sulfur, chloride and fluoride. In addition to these contaminants, the process gases contain dust, and volatilized oil from the mill scale. The dust produced in the sintering process is drawn through wind boxes beneath the traveling grates into the gas main where large particles drop out into a series of dust hoppers. In order to control the dust generated at the various points, de-duster systems are also operated which utilize wet scrubbers. Sludge draining from the scrubbers of the de-duster systems flows by gravity to the sinter plant clarifier.

The wet scrubbers for cleaning the wind boxes and the gases of the de-duster systems constitute the sources of process waste water in the sinter plant. The contaminants of the waste waters consist of suspended

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[4] J. W. Schroeder and A. C. Naso, Iron and Steel Engineer, 1976, p. 60-66.

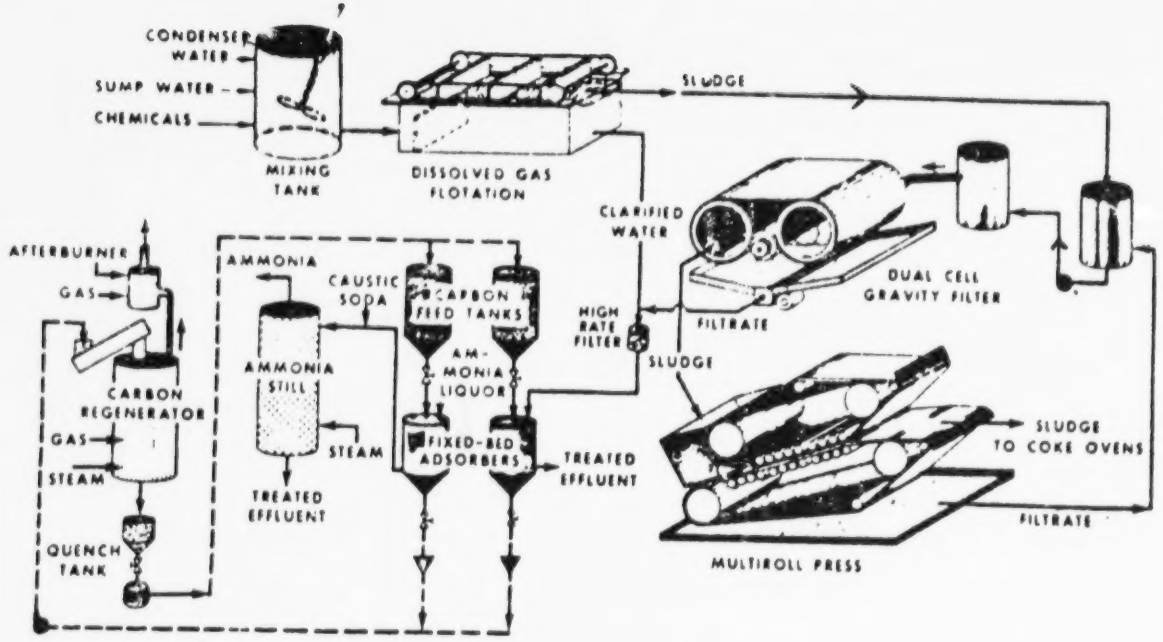

FIGURE 2. A MODULAR SYSTEM FOR COKE PLANT PROCESS WATER TREATMENT

[TAKEN FROM "A NEW METHOD OF TREATING COKE PLANT WASTE WATER", J.W.SCHROEDER AND A. CHARLES NASO, IND. STEEL ENGR., P. 60-66 (1976)]

TABLE 2. VARIATIONS IN THE CHARACTERISTICS OF WASTE AMMONIA LIQUOR*

Company	Waste Generated (liters/tonne) Total/Wal		pH	Total Ammonia mg/l	Total Cyanides mg/l	Phenol mg/l
1		175	8.7	5500	100	3000
2	275	192	9.1	2800	140	400
3	374	160		9841	10	1753
4	303	163		6500	65	1690
5	1943	167	8.5	5000	50	2500
6**	346	150	6.5-8.5	1500	15(1400)	550
7	343	196	7.5-8.5	3900	10-100	200-300
8	626	125	5.5	2500	4	200
9	251	138				350
10	417			3010		770
11			8.8-9.1	1713-3417	10-200	660-840

*Taken from Carnegie Mellon Institute Report: "An Evaluation of EPA-recommended technology for the treatment and control of Waste Waters from by-product coke plants", G. M. Wong Chong, S. C. Caruso and T. G. Patarlis.

**The value in parenthesis is thiocyanate.

solids (mainly iron oxide), oil and grease and acidity. Depending upon the nature and composition of the feed mixture for the sintering process, the concentrations of the contaminants and pH vary.

The currently practised waste treatment technology for the sinter plant waste waters consists of (i) removal of suspended solids in a clarifier by the addition of appropriate polyelectrolytes. The under flow from the clarifier is vacuum-filtered within the sinter plant and the filtered cake recharged to the sinter furnace. In a recirculating system the over flow is re-used after the necessary blowdown followed by make-up water additions. A schematic for the waste-water[7] recirculating system reported by Krikau and DeCaigny is shown in Figure 3 for the purpose of illustration. Typical data on the flow and chemical parameters reported earlier by the Interlake Corporation are presented in Table 3 for the purpose of illustration only[6].

POTENTIAL SCALING AND CORROSION CONDITIONS AND THEIR CONTROL

In the sinter plant, conditions of high basicity sinter often exist when the lime and magnesia contents of the dusts in the sinter plant scrubbers becomes high and consequently the scrubber water pH exceeds 12. The current method for controlling scaling and corrosion in the scrubber water treatment and recycle system is through the addition of acid and blow down and thereby controlling the chemical stability of the water (Ryznar Index). In this method, severe corrosion might be brought about by increased acid additions and decreased blow down rate. With decreased acid addition, a concommitant high increase in blow down rate is necessary to bring Ryznar index to the range of 5-7 and thus prevent conditions of scale formation. Under conditions of zero discharge, the above method of corrosion and scale control may present problems. It is felt that research and development efforts should be directed toward the development of suitable additives for deactivating the chemical scale-forming metal ions and at the same time controlling the pH and affording corrosion protection.

BLAST FURNACE

The production of iron from iron ores and other iron-bearing materials is carried out in the blast furnace. The iron-bearing materials, coke and limestone (and dolomite) are charged into the top of the blast furnace and hot air is blown into the bottom. Reducing gases from the coke (and from the liquid or gaseous fuels injected with the air blast at the tuyers) react with the oxygen of the iron ores and form porous iron. The fluxes (limestone and dolomite) react with the impurities in the charge (burden)

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[7] Fred. G. Krikau and Roger R. DeCaigny, San Francisco Regional Technical Meeting of the Amer. Iron and Steel Inst., 1970.

[6] R. E. Touzalin, "Pollution Control of blast furnace plant gas scrubbers through recirculation", Interlake Steel Corporation's report prepared for U.S. EPA, Project 12010.

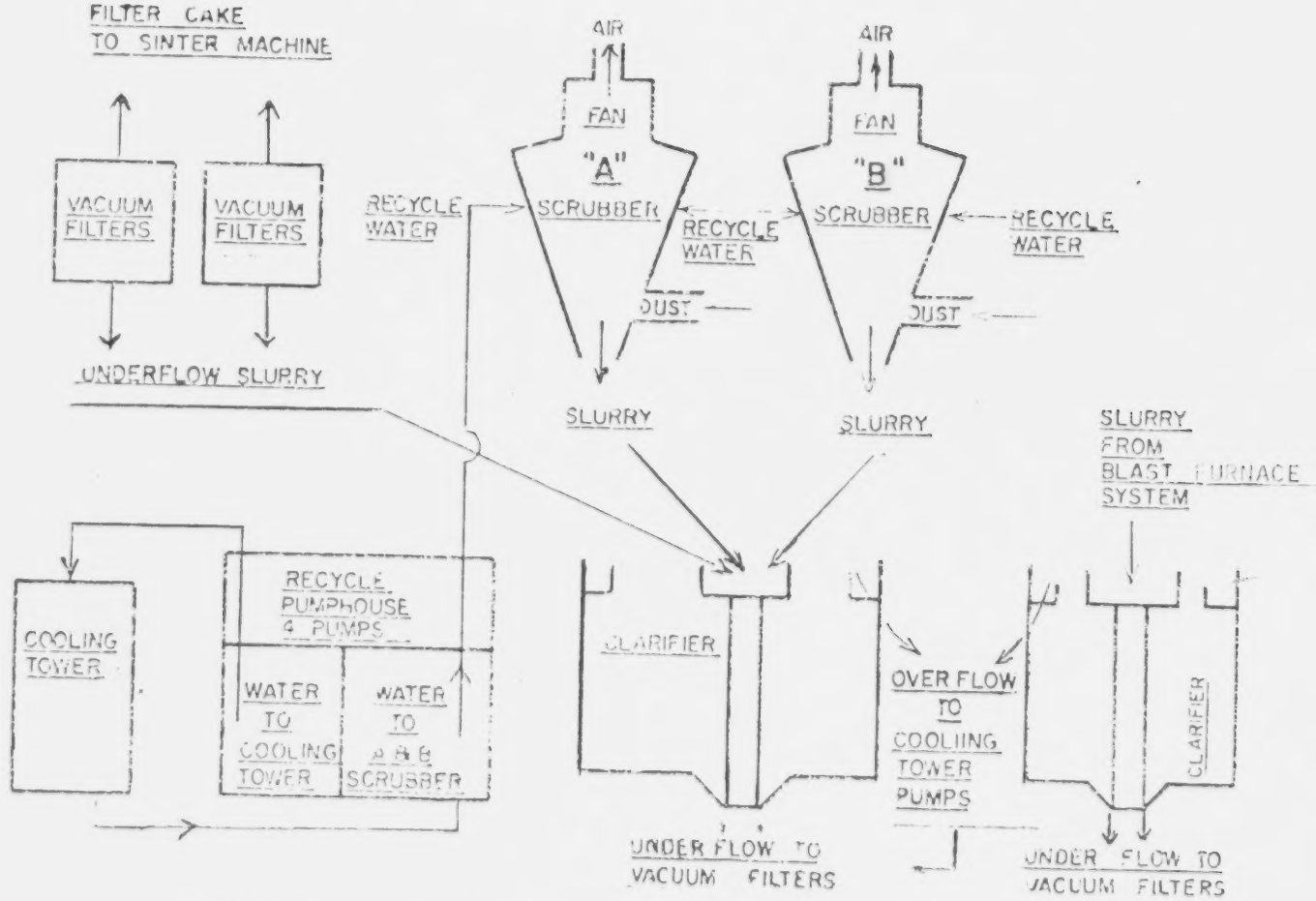

FIGURE 3. SINTER PLANT PROCESS WATER TREATMENT AND RECYCLE

(TAKEN FROM F.G.KRIKAU AND R.R.DE CAIGNY, SAN FRANCISCO REGIONAL TECHNICAL MEETING OF THE AMER. IRON AND STEEL INST., 1970)

TABLE 3. SINTER PLANT SCRUBBER WATER RECIRCULATING SYSTEM*

Balanced Condition Parameters

Location	Flow liters/ min	Suspended Solids kg/tonne of Iron Produced	Ammonia Nitrogen kg/tonne of Iron Produced	Cyanide kg/tonne of Iron Produced	Phenol kg/tonne of Iron Produced	Iron kg/tonne of Iron Produced	pH
Make-up Water	1363	0.043	0.002	0.00001	0.000009	0.0013	8.1
Clarifier Influent	2612	19.16	0.053	0.043	0.0014	7.2	10.5
Clarifier Effluent	2385	0.47	0.036	0.011	0.000025	0.042	11.0
Clarifier Underflow	190	18.7	0.002	0.032	0.0013	7.15	11.2
Blow-Down	1136	0.22	0.018	0.006	0.000011	0.02	11.0
Evaporation Loss	38						

*Taken from "Pollution Control of blast furnace plant gas scrubbers through recirculation", R. E. Touzalin, Interlake Steel Corp. Rep. prepared for EPA Project 12010.

to form the slag. Molten iron collects in the hearth of the furnace and molten slag forms a pool on the top of the molten iron. Periodically, the furnace is tapped and iron and slag are withdrawn. An important by-product of the blast furnace process is its exhaust gas which is used as a fuel for preheating the hot blast in the stoves and as supplemental fuel for boilers.

The blast furnace gas is wet-scrubbed (i) to remove particulate matter from the gas (ii) to reduce its moisture content and thus increase its BTU value. Besides the suspended solids, the significant pollutants in the blast furnace gas scrubber water are cyanide, phenols, ammonia, temperature and pH. The particulate matter escaping into the blast furnace gas (and subsequently removed by wet-scrubbing) consists of (i) oxides of iron, $CaCO_3$, CaS, $MgCO_3$, SiO_2, CaO, MgO, KCN and carbon. The scrubbing water attains alkaline pH's through its turbulant interaction with the alkaline minerals and chemicals in the fumes and dust in the top gases of the furnace. Further because of its absorption of the thermal energy from the hot gases, the gas cleaning water gets thermal pollution. Data on the water characteristics of the blast furnace sampler water recirculating system reported earlier in the literature[6] are presented in Table 4 for the purpose of illustration only.

A schematic of the blast furnace gas cleaning water recycle system taken from Interlake's report[7] is shown in Figure 4 for the purpose of illustration. Generally, the gas-cleaning system operates under positive pressure from the blast furnace. After 50 to 75% of the particulate matter in the blast furnace gas in removed by the dust catchers, about 99% of the residual particulates are collected by the venturi scrubber followed by a mist eliminator or separator. Finally, the gas cooler tower where the flow is subjected to water sprays to cool the gas and condense any moisture in excess of saturation. In the recirculating system the venturi pumps send the gas-cleaning water to venturi scrubbers where the particulates are picked up. The gas cooler water picks up the heat from the blast furnace gas. Effluents from the venturi and gas cooler are then combined and they flow to the clarifier (thickener). Here the suspended solids are removed by gravity and by using chemicals and polyelectrolytes. The resulting sludge is either removed as such or are subjected to vacuum filtration. The process water over-flow from the thickener flows to the hot well from where it is sent to the cooling tower. Finally the process water from the cooling tower goes to the cold well. To control the dissolved solids in the system, part of the water is blown down either to a terminal treatment plant or to the source rivers, lakes or municipal sewers. Make-up water from either of the raw water sources (rivers or lakes)

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[6] R. E. Touzalin, "Pollution Control of blast furnace plant gas scrubbers through recirculation", Interlake Steel Corporation's report prepared for U.S. EPA, Project 12010.

[7] Fred G. Krikau and Roger R. DeCaigny, San Francisco Regional Technical Meeting of the Amer. Iron and Steel Inst., 1970.

TABLE 4. BLAST FURNACE SCRUBBER WATER RECIRCULATING SYSTEM*

Balanced Condition Parameters

Location	Flow liters/ min	Suspended Solids kg/tonne of Iron Produced	Ammonia Nitrogen kg/tonne of Iron Produced	Cyanide kg/tonne of Iron Produced	Phenol kg/tonne of Iron Produced	Iron kg/tonne of Iron Produced	pH
Make-up Water	2460	0.08	0.0036	0.000015	0.000015	0.0023	8.1
Clarifier Influent	17034	8.65	0.53	0.0625	0.00085	3.95	8.2
Clarifier Effluent	16277	0.35	0.51	0.037	0.00002	0.08	8.3
Clarifier Underflow	492	8.3	0.016	0.026	0.00065	3.85	8.5
Blow-Down	1703	0.035	0.053	0.0038	0.00002	0.009	8.3
Evaporation Loss	265						

*Data taken from "Pollution Control of blast furnace plant gas scrubbers through recirculation", R. E. Touzalin, Interlake Steel Corp. Rep. Prepared For EPA Project 12010.

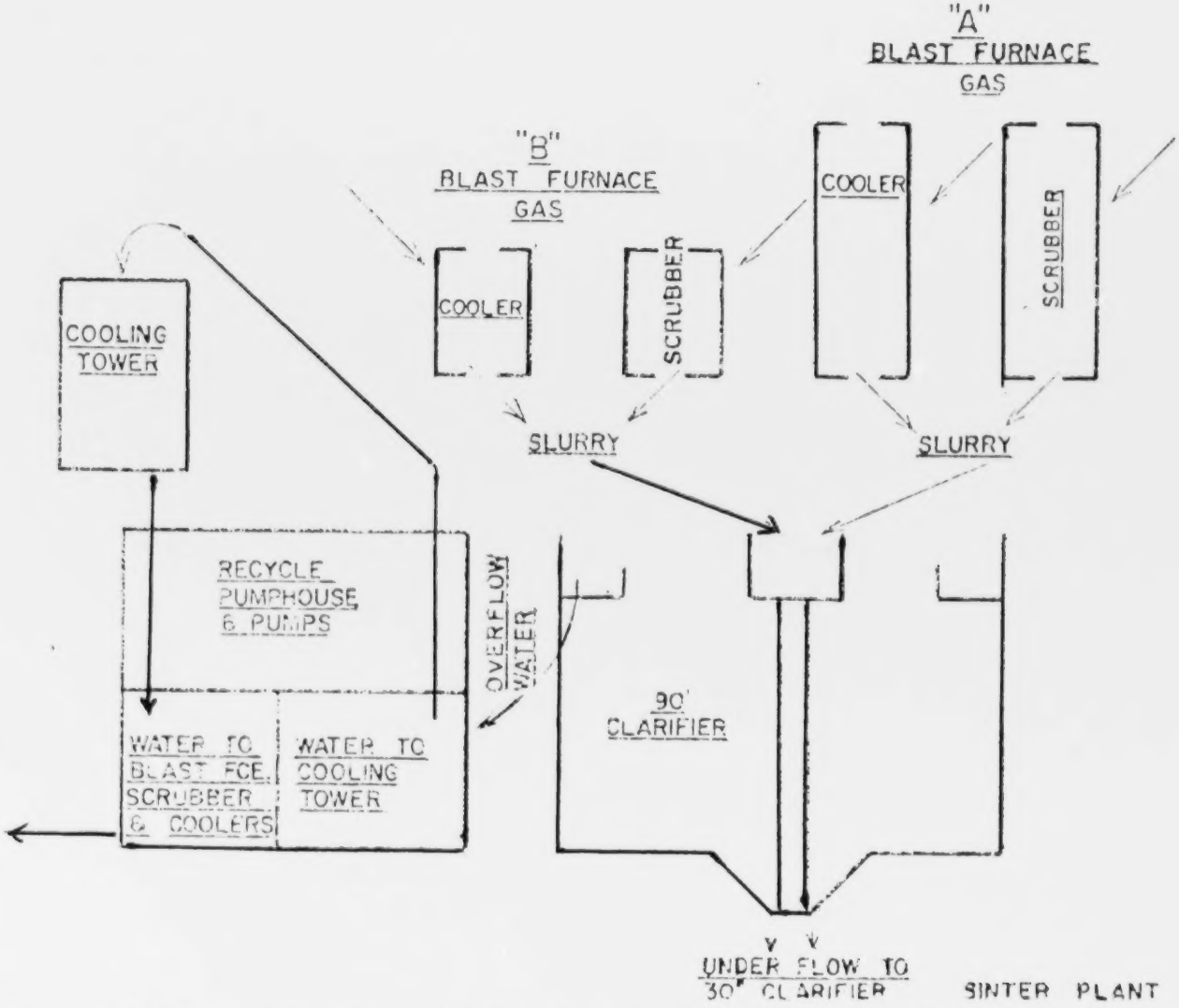

FIGURE 4. PROCESS WATER TREATMENT AND RECYCLE FOR BLAST FURNACE
(TAKEN FROM P.A. KIRAU AND R.P. DE CAIGNY, SAN FRANCISCO REGIONAL MEETING OF THE AMER. IRON AND STEEL INST., 1970)

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is then added to the cold well to compensate for the blow down and other process losses. Finally, water from the cold well is recirculated to the venturi scrubber and the gas cooler. The process water recycle system can be one of two types, viz., combined venturi and gas cooling system or segregated cascading system.

The above discussion does not include the waste waters that are used for cooling various parts of the blast furnace such as the tuyers, bosh, and hearth stoves. These waters do not pick up any chemical pollutants or particulates, although their thermal load is increased. Depending upon the overall water problems of a given iron and steel plant the systems for handling the cooling waters would be using a once-through operation and recirculating, cooling and appropriate water treatment, with or without provision for blow down into the gas-cleaning and gas-cooling systems.

The treatment of process waters from gas-cleaning and gas-cooling operations on a recirculating basis consists of (a) collecting the effluent waters (b) precipitating the suspended solids in a clarifier, (c) passage of the clarifier overflow through cooling towers to reduce the heat load, (d) controlling the chemical stability of the process water stream by blow-down and acid addition in order to prevent scaling and corrosion, and (e) recirculation of the treated water to gas-cleaning and gas-cooling operations. Besides, polyelectrolytes, dispersants, anti-scaling, anti-corrosion and anti-fouling chemicals are added to the recirculating water systems at the appropriate stages. The waste-treatment methods of the recirculating systems do not include removal of dissolved solids such as sodium, chloride, calcium, magnesium, iron, carbonate, sulfate and the contaminants such as ammonia, phenol, cyanide and control of pH. The prediction and control of the chemical stability of this system of dissolved solids is a major problem of the recycle operation. This problem is currently being managed through blow-down and make-up.

SCALING AND CORROSION PROBLEMS AND THEIR CONTROL

In blast furnace gas cleaning systems on recycle, the following major failures due to scaling have been observed: (a) plugging of spray nozzles, (b) deposits in venturi throats and (c) closing of the supply pipes by precipitated materials. These materials have been identified as being mainly calcium carbonate. The tendency of the system for calcium carbonate scaling is currently being determined through the use of the Ryzner Stability Index (RSI) or the Langelier Saturation Index (LSI). In the LSI system, a zero index denotes that the system is in equilibrium with calcium carbonate. A positive index indicates scaling tendencies and a negative index indicates corrosive trends. When Ryzner stability index (RSI) is higher than 7.5 to 8.0 a corrosion condition is indicated. RSI values lower than 6 indicate scaling tendency. Values of 6 to 7 will indicate non-scaling and non-corrosive conditions. In view of the contribution of calcium and alkalinity from the limestone in the flux, and the carry over of calcium chloride, the potential for calcium carbonate exists whenever the solubility limits are exceeded in the blast furnace gas cleaning recycle system. The addition of sulfuric acid to control alkalinity may potentiate calcium sulfate scaling. The control of scaling and corrosion in the blast furnace

waste water recycle system is currently being managed by means of blow down and addition of acid and thereby bringing the Ryzner Stability Index (or the Langelier Saturation Index) to the desired range.

R&D efforts are warranted for the development of low-cost non-polluting scale-inhibitors that would inactivate Ca, Mg and Fe through sequestration. By this means the quantity of acid added may be lessened and thus prevent corrosion conditions.

STEEL MAKING PROCESS

The three major methods currently in use in the USA for the production of steel are: the basic oxygen furnace, the open hearth furnace and the electric arc furnace. In each of these methods, the raw materials consist of hot metal (iron), scrap steel, limestone, burnt lime (CaO), fluorspar (CaF_2) and dolomite ($MgCO_3$ and $CaCO_3$). Slag, smoke, fume and waste gases are the waste products. In all the three methods pure oxygen and/or air is used to refine raw iron through the oxidation of the impurities such as silicon, carbon, phosphorus and magnanese. Since all the three steel making processes commonly have two types of waste waters, viz., non-contact cooling waters and the gas-scrubbing waters, we are presenting a detailed discussion of the BOF operation only.

The basic oxygen furnace is a pear-shaped, refractory-lined open mouth construction. The furnace is supported on trunnions mounted in bearings and is rotated for tapping of steel ladles and dumping of slag. The charge consists of a mixture of pig iron (70%), scrap metal (30%) and fluxes. Oxygen is injected into the furnace through copper-tipped steel lances to bring about the oxidation of impurities. The waste products of this process are heat, airborne fluxes, slag, carbon monoxide and dioxide gases and oxides of iron emitted as submicron dust. The waste water discharge sources of a BOF plant consists of non-contact cooling water and the gas cleaning process water. The non-contact cooling water is from the cooling of the hoods and the lances. It is not contaminated except for the heat load. This can be recirculated after being cooled and treated with inhibitors for corrosion and bacterial fouling. Alternately, it can be utilized in the gas-cleaning system. The gas cleaning process waters are derived from the quencher, the venturi scrubber and the wet precipitator units.

The water treatment of the BOF gas-cleaning recirculating waters consists of collecting the effluent water in a thickener, removal of the suspended solids by gravity and through the addition of polyelectrolyte and the recycle of the thickener overflow water back to the gas-cleaning units. Inhibitor compounds are added to the recirculating waters for controlling scaling, corrosion and bacterial growth. By means of a small blow down, the dissolved solids content of the recirculating water system is controlled.

The BOF waste water system of the recirculating type is illustrated by the flow diagram (Figure 5) provided by one of the steel mills visited by us. The system consists of two process water loops and two indirect

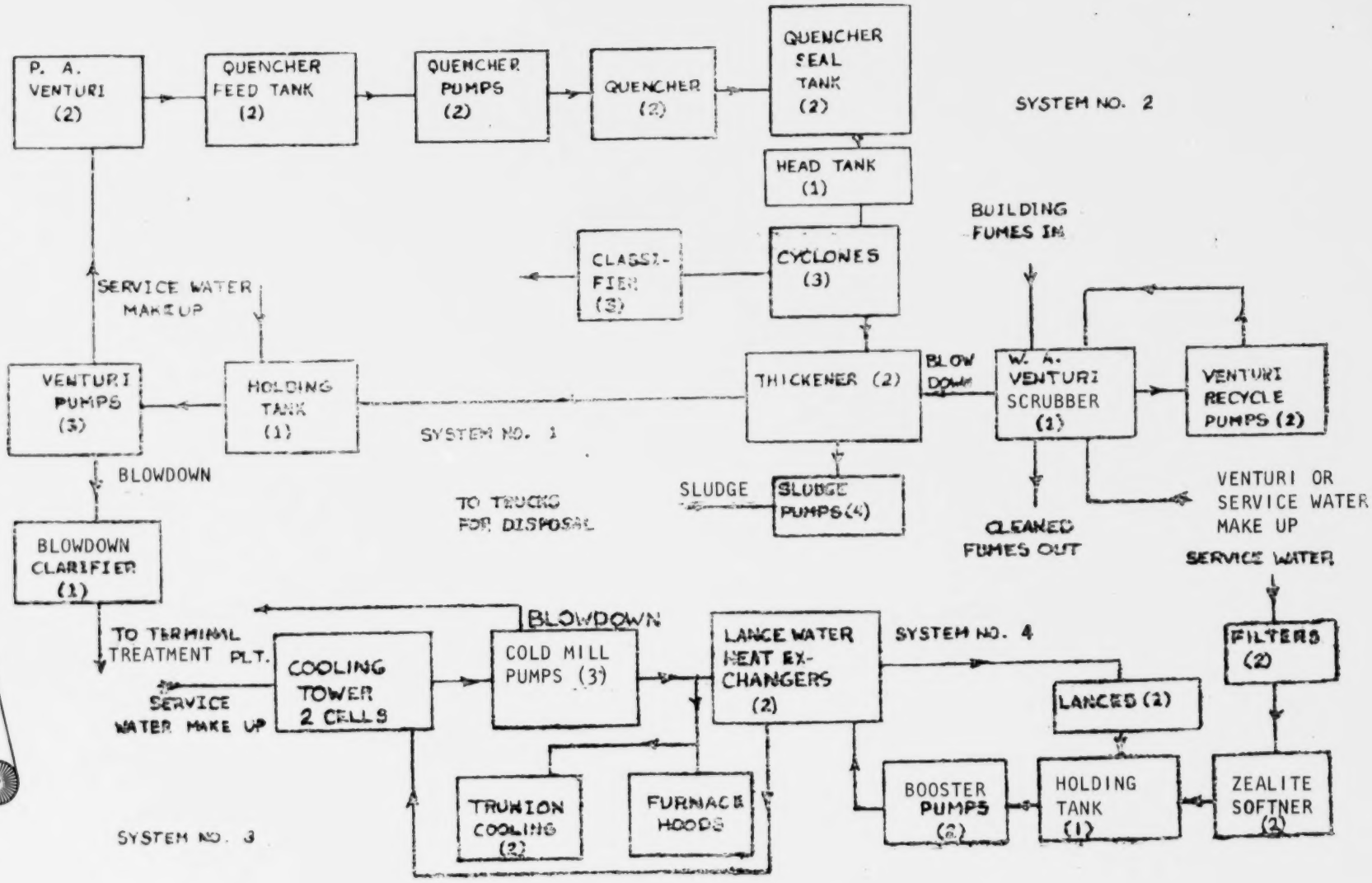

FIGURE 5. WATER FLOW DIAGRAM FOR BOF SYSTEM

(OBTAINED THROUGH THE COURTESY OF INLAND STEEL COMPANY'S WASTE WATER TREATMENT FACILITY)

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cooling water loops. System number 1 is for cooling and scrubbing the gases evolved from the steel making furnaces. System number 2 is a scrubbing loop for cleaning building fumes. System number 3 and number 4 are for non-contact cooling of the furnace hoods and lances.

SCALING, CORROSION, FOULING AND FOAMING

The non-contact cooling waters of the recirculating type are treated chemically for corrosion control. The corrosion inhibitors are of a proprietary nature. However, it is gathered that non-chromate type of inhibitors are in use. One such class of compounds are the aminophosphonates, which serve the dual role of scale and corrosion inhibition. In the case of the use of cooling towers, different biocides are being used for eliminating biological growth. For scale prevention, nearly all the water treatment companies appear to use aminophosphonates.

As a result of our discussions with the water treatment companies, it has been found that in a number of operations adopting the recirculating systems, severe problems of chemical deposit (scale) formation and pluggage at the return lines, venturi throats and the recycle lines from the venturi to the quencher are not too uncommon. The deposits have the compositions, $CaCO_3$ - 50%, Fe-oxides - 35%, CaF_2 - 5%. This problem has been occurring in spite of their present treatment practices. The build up of total dissolved solids, pH variations and finely divided suspended solids contribute to this problem. The current method of control of this problem is through the control of the chemical stability of the system in combination with the addition of scale inhibitors and dispersants. However, since the stability index method currently being used (as a measure of the chemical stability of the waters) is based upon largely calcium, and total alkalinity, and does not take into account the chemical interactions of iron and the surface charge neutralization of the finely divided suspended solids, this method therefore may not be adequate and effective. Under conditions of Zero discharge, the problem of the dissolved solids in the recirculating waters would be magnified considerably. Hence R&D efforts directed toward solving this problem are necessary.

CONTINUOUS CASTING

Billets, blooms, slabs and other shapes are cast by flowing hot steel from teeming ladles into the continuous casting molds. The casting molds are water-cooled. On being discharged from the mold, the cast product is cooled in a spray chamber. The product is then cut to desired length in subsequent sections of the continuous casting mill. The water systems serving the continuous casting process consist of mold cooling, spraying and machine cooling water systems. For the mold and machine cooling, closed recycle water systems are used, and the spray water system is an open recycle system. Mold cooling uses high purity water (zeolite-softened) because of the requirement of the high heat transfer rates through the mold wall. The problems associated with the mold cooling water systems include the formation of calcium carbonate scale, migratory corrosion products, suspended solids, organics and biological fouling. In Table 5 are illustrated the various deposits encountered in the mold cooling system and their

nature and causes.

TABLE 5. MOLD DEPOSITS WITH NATURE AND CAUSES*

	CASE I	CASE II	CASE III
Silica as SiO_2, %	4	1	4
Iron as Fe_2O_3, %	1	85	8
Loss on Ignition, %	7	9	29
Phosphate as P_2O_5, %	7	-	28
Calcium as CaO, %	38	-	16
Magnesium as MgO, %	2	-	7
Carbonate as CO_2, %	31	-	-
Zinc as ZnO, %	-	-	-
Chromate as Cr_2O_3, %	-	5	4

Case I - Calcium Carbonate Scale Poor Softener Operation (Closed System)

Case II - Migratory Corrosion Products (Closed System)

Case III - Severe Hydraulic Fluid Leaks (Open Recirculating Tower System)

*Taken from D. J. Juvan, "Design of Critical System For Continuous Casters," paper presented at the 1975 AIME-Natl. Open Hearth And Basic Oxygen Steel Conference, Toronto, Canada, April 1975.

Current water treatment practices comprise (1) the softening of the influent water by means of ion exchange (Zeolite softener operation) to bring the water hardness to less than 10 ppm (to prevent calcium carbonate scaling), (2) effective skimming of any oil and grease that infiltrate the recirculating system (3) installing filters and strainers in the system prior to the mold, (4) the use of corrosion inhibitors, such as the chromates, nitrites, phosphates and zinc-bearing compounds, and (5) the use of proprietary biocides for the control of biological growths.

Under the conditions of the 1983 guidelines, it would appear that the currently practised methods of water treatment might be largely sufficient except that non-chromate type inhibitors should be substituted. Further, open cooling towers should preferably be eliminated from the recirculating water system so that atmospheric contamination, corrosion and fouling problems associated with them could be obviated.

The spray water system gets contaminated most among the three systems. The contaminants include iron oxide scale, oil, grease and other foreign objects. Because of the use of recirculating cooling tower systems, airborne contaminants, corrosion and biological fouling constitute the

additional contaminants. As a result of these contaminants, the major problem encountered in the spray water system is fouling and plugging of spray nozzles. The spray cooling recirculating system[8] is schematically illustrated in Figure 6.

Various types of deposits which have been found to plug up the spray nozzles and headers[8] are illustrated in Table 6.

The current practice for water treatment in the spray water recirculating system consist of (a) settling of the heavy solids and the iron oxide scales, (b) skimming of the oil and grease (c) sedimentation of the finely divided solids through the additions of polyelectrolytes or (d) high-rate sand filters, (e) the addition of corrosion inhibitors and microbiocides and (f) installation of on-line filters. These methods should be adequate for the treatment of recirculating systems under the zero discharge conditions required by the 1983 EPA guidelines. However, the use of non-chromate type of corrosion inhibitors and non-polluting dispersants for the avoidance of the "nozzle-plugging" problem should be instituted.

The machine cooling water system services several pieces of equipment. It also cools the mold water through a heat exchanger. In the recirculating system for the machine cooling waters, open cooling towers are often installed in the circuit[8] as illustrated in Figure 7. The contaminants picked up by this water system are similar to those of the spray water system. High quality water is required for this system in view of its heat exchanger use. The current treatment methods include sedimentation of any suspended solids, installation of filters in the circuit and the addition of corrosion inhibitors, deposit control agents and microbiocides. Excepting for the use of non-chromate inhibitors, the present methods should be effective and compatible under the zero discharge condition of the 1983 guidelines.

HOT MILLS

In all integrated steel mills, steel slabs are put through a hot-strip rolling process. In this process the slab, sheet, bloom billet or bar is being oxidized, cooled and washed with a high pressure water spray. The layer of iron oxide (mill scale) formed on the entire surface of the steel, as it is being rolled, is broken away from the steel. It then falls through the roll tables into the flume or sewer through which high velocity water is flowing. Large amounts of lubrication greases and oils from the rolling machinery as well as other mill debris find their way into the flume. The principal contaminants in the effluents from the hot mills are mill scale, oil and grease. The quantity of scale produced is estimated at about 3% of the output of the mill. The volume of water used in the hot forming operation, the nature and quantities of the mill scale in the waste waters varies widely with different steel mills.

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[8] D. J. Juvan, "Design of Critical System for Continuous Casters", paper presented at the 1975 AIME-National Open Hearth And Basic Oxygen Steel Conference, Toronto, Canada, April 1975.

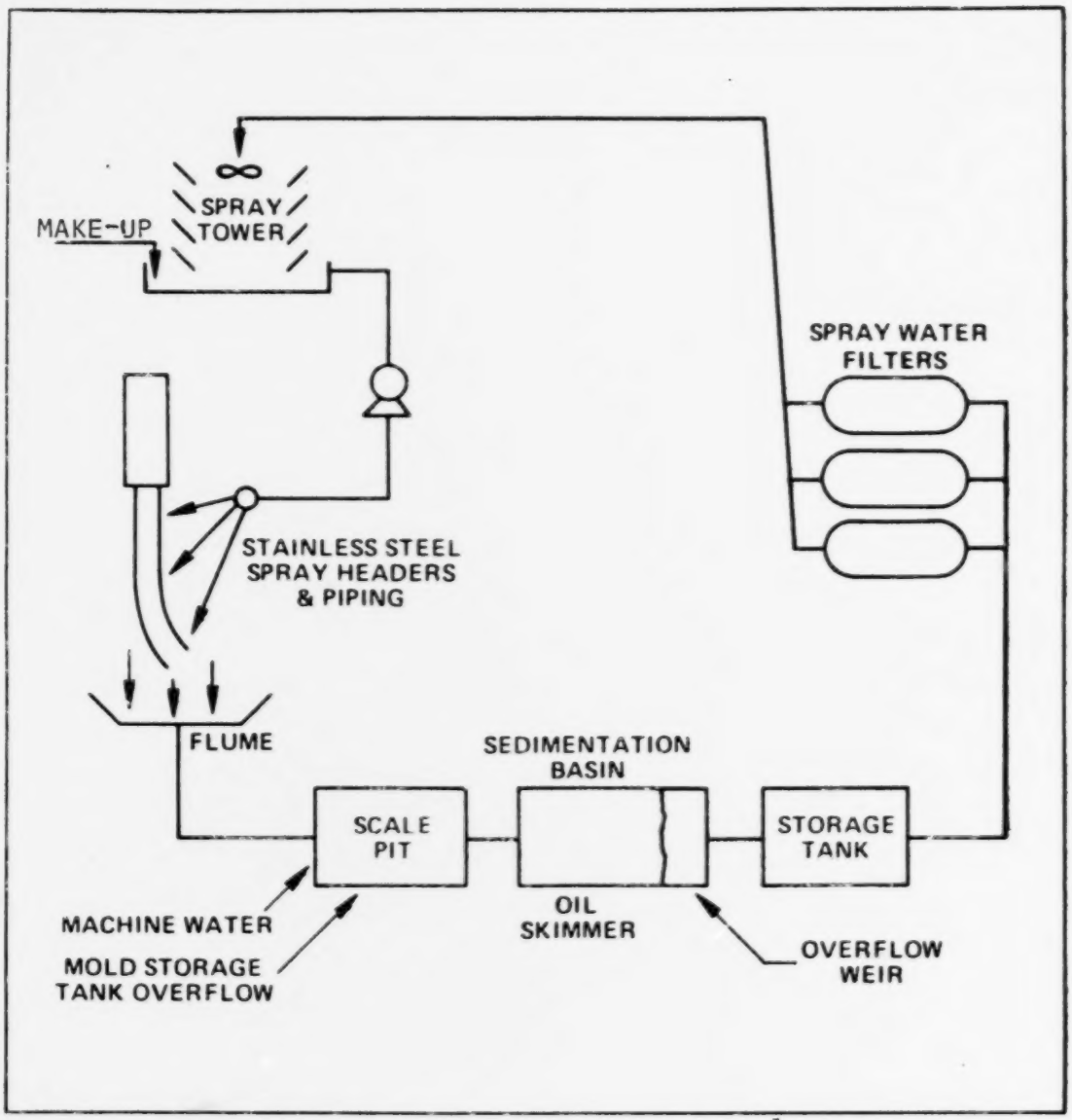

FIGURE 6. SPRAY-COOLING RECIRCULATING SYSTEM

[TAKEN FROM, "DESIGN OF CRITICAL SYSTEM FOR CONTINUOUS CASTERS", BY D.J. JUVAN, 1975 AIME-NATL. OPEN HEARTH AND BASIC OXYGEN STEEL CONFERENCE, TORONTO, CANADA, APRIL 1975.]

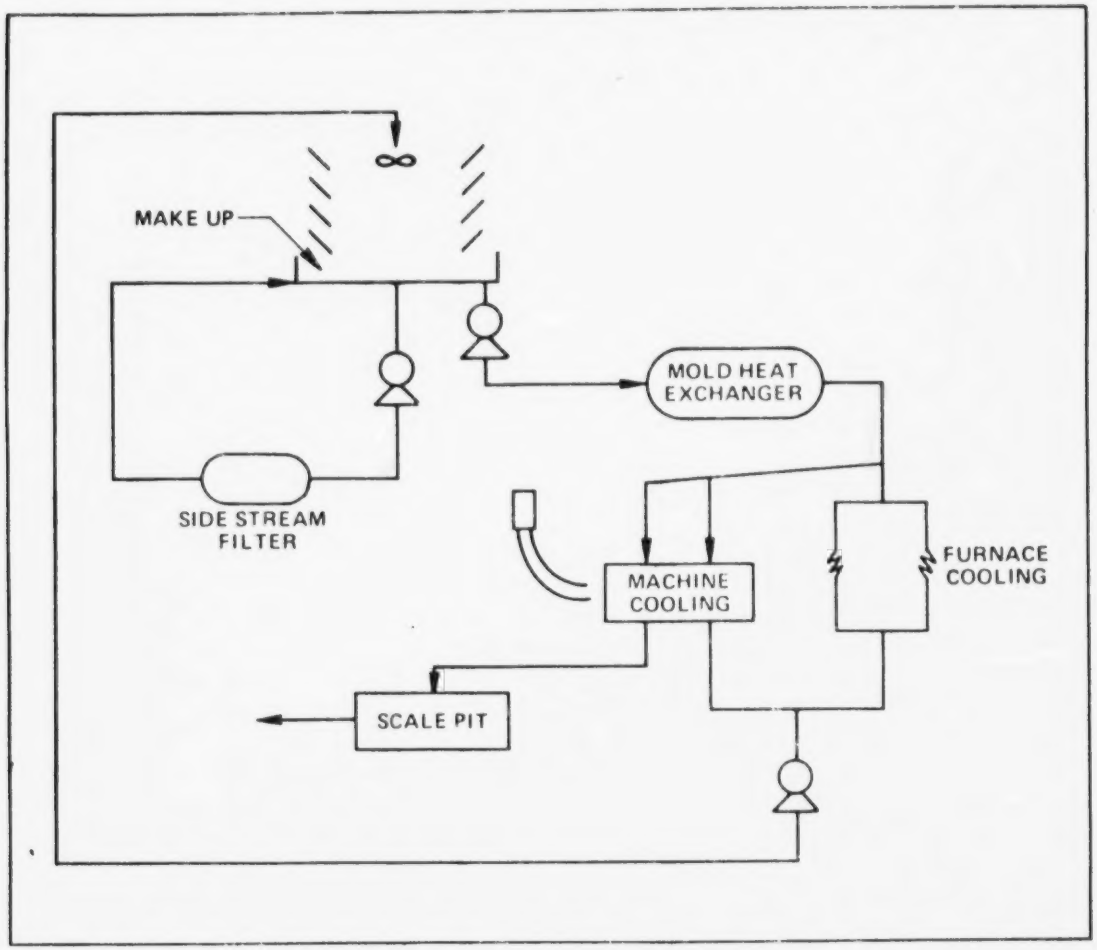

FIGURE 7. TREATMENT AND RECIRCULATION SYSTEM FOR MACHINE COOLING WATERS

[TAKEN FROM, "DESIGN OF CRITICAL SYSTEM FOR CONTINUOUS CASTERS", BY D.J. JUVAN, 1975 AIME-NATL. OPEN HEARTH AND BASIC OXYGEN STEEL CONFERENCE, TORONTO, CANADA.]

TABLE 6. TYPES OF DEPOSITS THAT CAN PLUG SPRAY NOZZLES AND HEADERS*

Constituent, %	CASE I	CASE II	CASE III
Silica, SiO_2	1	3	8
Aluminum, Al_2O_3	-	1	5
Iron, Fe	79	68	13
Loss on Ignition	4	19	65
Phosphate, P_2O_5	1	-	2
Magnesium, MgO	1	-	1
Zinc, ZnO	2	4	4
Sulfate, SO_3	-	3	-
Calcium, CaO	7	1	2
Carbonate, CO_2	5	1	-

Case I - Corrosion of System Piping and Headers

Case II - Unsatisfactory Oil and Scale Removal

Case III - Biological Fouling (30-40% Bacterial Slime)

*Taken from "Design of Critical Systems For Continuous Casters", by D. J. Juvan, 1975 AIME Natl. Open Hearth and Basic Oxygen Steel conference, Toronto, Canada.

11000 - 38000 liters of water per tonne of steel rolled might be applied in this operation.[9-12]

The hot mill operation generate two types of waste waters, viz., waters from the furnace cooling and process waters from the hot rolling operations. The furnace cooling waters do not get contaminated except for heat load. Depending upon the water problems of the individual steel mills, the furnace cooling water can be cooled, treated for corrosion inhibition and recirculated; or else blown down into the recirculating process waters of the hot rolling operations.

The treatment of the process waste waters from the hot mill operations briefly consists of (1) collecting the waste waters in a scale pit, (2) removing the scales by gravity settling, (3) removal of the oil by means of an oil skimmer, (4) removal of the finely divided scales, suspended solids and oil by using a deep-bed sand filter (5) passage of the treated water through cooling tower to reduce the thermal load and (6) recirculate the water to the hot-strip mill after a small blow down in order to control the dissolved solids content of the recirculating water.

The chemical additives to the recirculating water system consist of (1) polyelectrolyte feed to flocculate the finely divided scales and other suspended particulates (2) acid and other descaling compounds to control the chemical stability of the water (Ryzner Stability Index) and (3) chemicals for controlling bacterial growth and foaming.

PROBLEMS OF SCALING, CORROSION AND FOULING

On the basis of a review of the published data and discussions with the environmental control personnel of the steel mills that we visited, it appears that no serious corrosion problems are encountered under the recirculating conditions of operation at present. The formation of deposits and chemical scales is a problem which is being controlled through the addition of scale inhibitors and dispersing compounds recommended by the water treatment companies. Under zero discharge conditions of the 1983 EPA effluent guidelines, it is expected that the problem of chemical scale formation might be more severe due to potentially increased dissolved solids and finely divided suspended solids content of the recirculating waters and the lack of automatic monitoring and control of the chemical stability of the waters. R&D efforts directed toward the development of an effective method for chemical stability of aqueous systems should be undertaken.

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[9] J. P. Gravenstreter and R. J. Sanday, Iron and Steel Engineer, 46, 85 (1969).

[10] C. Browman, Blast Furnace Steel Plant, 59, 19 (1971).

[11] R. S. Patton, Iron and Steel Engr., 48, 98 (1971).

[12] R. Nebolsine, Iron and Steel Engr., 48, 85 (1971).

PICKLING WASTE WATERS

Since a large percent of the steel products produced in an integrated steel mill undergo acid pickling for removing the scale, the problem of handling the spent pickle liquor and the rinse water, their treatment for re-use or safe disposal is of great importance. Either sulfuric or hydrochloric acid is used in the acid baths. The waste waters from the pickling operation consist of spent pickle liquor, acid rinse water and fume scrubber water. From published data, it is known that the spent pickle liquor contains 6-12% iron, 1-11% free acid, traces of heavy metals, oil and suspended solids[1]. Several methods are currently being practiced by the steel industry for handling this waste, i.e., (1) regenerating the acid (HCl or H_2SO_4) and recycling it to pickling operations, (2) deep well injection, (3) use as a source of iron and iron compounds (4) use for removal of phosphate from municipal sewage plants and (5) precipitating the iron through neutralization followed by removal of the precipitate and discharging the clarified effluent into rivers and streams. The feasibility of a closed loop system for the treatment of the waste pickle liquor was recently reported.[13] The closed-loop system consists of (a) a low temperature crystallization of $FeSO_4 \cdot 7H_2O$ from sulfuric acid waste liquor, (b) ion exchange adsorption of the ferrous iron from the ferrous sulfate, (c) oxidation of the ferrous to the ferric iron, (d) stripping the adsorbed iron from the ion exchange by HNO_3, (e) hydrolysis of the Ferric nitrate to Fe_2O_3 and HNO_3 and (f) recovery and recycle of the HNO_3 back to the ion exchange unit. The sulfuric acid recovered from the crystallizer is recycled back to the pickling operation.

The rinse water wastes generated by acid pickling are neutralized with lime, allowed to settle and the effluent discharged into rivers and streams. The gummy sludge produced is disposed at remote land areas or into deep sea. All these methods of handling the pickle rinse water cause some degree of environmental problem. Nippon Steel Corporation of Japan[14] recently has developed a recirculating ion exchange method for the treatment of acid-rinse water generated in the pickling process.

Fume scrubber water system absorbs the corrosive mist and vapors given off from the surface of the acid-pickling baths. Water from this system is combined with spent acid-rinse wastes and treated for acid removal and recycling.

Neither the published literature nor discussions with the environmental control personnel of the different steel mills which we visited have brought out any problems of scaling or fouling. However, in view of the strongly acidic nature of the waste waters, several corrosion problems are

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[1] D. Kwasnowski, International Metallurgical Reviews, 20, 137-145 (1975).

[13] J. C. Peterson, EPA Report No. EPA-600/2-77-127, (1977); NTIS-PB-270-090.

[14] "The Kimitsu Ion Exchange System for pickle rinse water treatment", by Nippon Steel Corporation, 1975.

expected in the supply lines and in the process equipment. This problem can be controlled by appropriate surface treatments of the materials of construction and through the addition of suitable corrosion inhibitors.

In conforming to the 1983 EPA effluent guidelines, it is felt that the existing technology can adequately handle the controlling of the potential problems of corrosion and fouling.

COLD ROLLING

Since the cold rolling operations consist of removing the rust preventive oil coating from the steel strips and processing them in the presence of lubricants consisting of oil and water, the waste waters generated in this process contain both floating and emulsified oils, detergents, cleaning chemicals, mill scale and other suspended solids. The current waste treatment practices consist of (1) skimming the floating oil, (2) filtration through a multilayer sand and gravel filter to remove suspended solids and emulsified oil and (3) further removal of oil in a thickener.[15] Alternately, the waste waters are subjected to aeration and the floating oils are skimmed. The emulsified oils left in the waters are treated with acid together with ferric or aluminum sulfate (or chloride) to split the emulsion into oily and aqueous layers. After removing the oil, the pH of the system is raised to precipitate the iron (or aluminum), allowed to settle and filtered. The treated effluent is either sent to terminal treatment facility or discharged into the plant outfalls. The solid residue is disposed at distant land sites or into deep ocean. A schematic of the treatment of the cold-rolling waste waters taken from the published literature[1] is shown in Figure 8.

On the basis of the published data, it would appear that chemical scaling and corrosion might not be problems of critical concern in the currently practised methods. Biological fouling and foaming are encountered and the currently practised technology is adequate for their control. However, under conditions of zero discharge in accordance with the 1983 effluent guidelines, the recirculating system would show considerable build-up of dissolved solids and finely divided solids (chemically precipitated material) and oil and grease which in turn could be expected to result in deposit formation and pluggage. Further, finely divided solids from bacterial growth could present a problem in a recirculating system under zero discharge conditions. In the event of recycling the treated effluents, control of the chemical stability of the effluent waters and addition of dispersants and scale inhibitors should be considered.

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[15] C. R. Seymons and J. Water, J. Water Pollution Control Federation, 43, 2280 (1971).

[1] D. Kwasnowski, International Metallurgical Reviews, 20, 137-145 (1975).

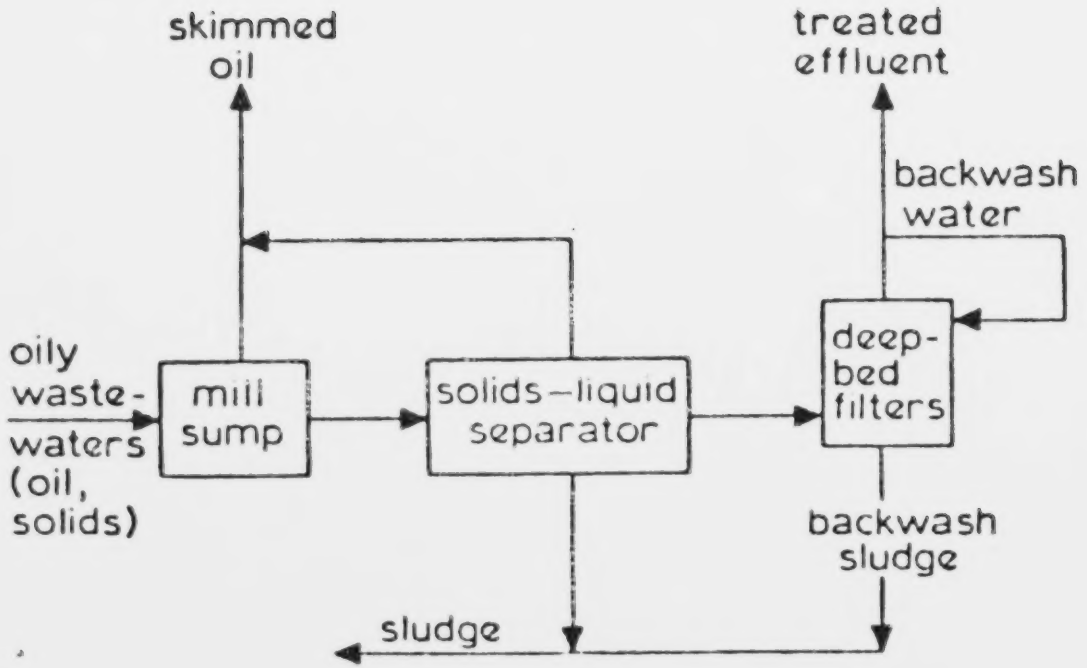

FIGURE 8. TREATMENT OF WASTE WATERS OF COLD-ROLLING OPERATIONS

[TAKEN FROM "WATER POLLUTION CONTROL IN AN INTEGRATED STEEL PLANT", BY D. KWASNOWSKI, INTL. METALURGY, REV., 20, 137-145 (1975)]

METAL COATING OPERATIONS

The metal coating operations include hot galvanizing, lead-tin alloy coating and, electrolytic plating of tin and chromium. The waste streams from these operations contain zinc, tin, fluorides, chromates, cyanides, acids and alkalis. Currently practised waste treatment methods consist of precipitation of the metals as their hydroxides, precipitation of the fluorides as the calcium fluoride and destruction of the cyanides by an alkaline chlorination method or alternately by biological oxidation methods. Ion exchange methods are also applied for the recovery of chromium from the waste waters[1,2]. Recently an innovative rinse-and-recovery system for metal finishing processes has been developed which consists of a two stage solvent spray rinse followed by a single stage aqueous immersion rinse with no plating solution exits to the sewer[16]. Although severe corrosion and scaling problems may not be encountered, the toxicity of the treated effluents is of great concern. Chromium, lead, zinc and cyanide are among the toxic components. Methods for their automatic (on-line) determination and control should be instituted into the recirculating system.

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[1] D. Kwasnowski, International Metallurgical Reviews, 20, 137-145 (1975).

[2] R. Nebolsine, Iron and Steel Engineer, 44, 122-135 (1967).

[16] W. C. Trnka and C. J. Novotny, EPA Report No. 600/2-77-099 (1977).

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APPENDIX A

EFFLUENT LIMITATIONS GUIDELINES OF U.S. EPA SET ON THE BASIS OF BPCTCA AND BATEA*

Subcategory	Pollutant Parameter	BPCTCA kg/kkg product		BATEA kg/kkg product	
		Maximum For Any One Day	Daily Average over 30 days	Maximum For Any One Day	Daily Average over 30 days
Coke-oven (By-product recovery process)	Cyanide	0.0657	0.0219	0.0003	0.0001
	Phenol	0.0045	0.0015	0.0006	0.0042
	Ammonia	0.2736	0.0912	0.0126	0.0042
	Oil and Grease	0.0327	0.0109	0.0126	0.0042
	Suspended Solids	0.1095	0.0365	0.0312	0.0104
	Sulfide			0.0003	0.0001
Beehive-oven Process	No discharge of process waste water pollutants to navigable waters				
Sinter Plant	Suspended Solids	0.0312	0.0104	0.0156	0.0052
	Oil and Grease	0.0063	0.0021	0.0063	0.0021
	Sulfide			0.00018	0.00006
	Fluoride			0.0126	0.0042
	pH		6.0 to 9.0		
Blast Furnace (iron)	Suspended Solids	0.0780	0.0260	0.0390	0.0130
	Cyanide	0.0234	0.0078	0.0004	0.00013
	Phenol	0.0063	0.0021	0.0008	0.00026
	Ammonia	0.1953	0.0651	0.0156	0.0052
	Sulfide			0.0005	0.00016
	Fluoride			0.0312	0.0104
	pH		6.0 to 9.0		

APPENDIX A (cont.)

EFFLUENT LIMITATIONS GUIDELINES OF U.S. EPA SET ON THE BASIS OF BPCTCA AND BATEA

Subcategory	Pollutant Parameter	BTCTCA kg/kkg product		BATEA kg/kkg product	
		Maximum For Any One Day	Daily Average over 30 days	Maximum For Any One Day	Daily Average over 30 days
Blast Furnace (Ferromanganese)	Suspended Solids	0.3129	0.1043	0.0780	0.0206
	Cyanide	0.4689	0.1563	0.0008	0.00026
	Phenol	0.0624	0.0208	0.0016	0.00052
	Ammonia	1.5636	0.5212	0.0312	0.0003
	Sulfide			0.0009	0.0052
	Manganese			0.0156	0.0052
	pH	6.0 to 9.0			
Basic oxygen Furnace (semi-wet air pollution methods)	Suspended Solids Fluoride pH	No discharge of process waste water pollutants to navigable waters.			
Basic oxygen Furnace (Wet Air Pollution control methods)	Suspended Solids	0.0312	0.0104	0.0156	0.0052
	Fluoride			0.0126	0.0042
	pH	6.0 to 9.0		6.0 to 9.0	
Open Hearth	Suspended Solids	0.0312	0.104	0.0156	0.0052
	Fluoride			0.0126	0.0042
	Nitrate (NO_3)			0.0282	0.0094
	Zinc			0.0030	0.0010
	pH	6.0 to 9.0		6.0 to 9.0	
Electric Arc Furnace (Semi-wet air pollution control)	Suspended Solids Zinc Fluoride pH	No discharge of process waste water pollutants to navigable waters			

APPENDIX A (cont.)

EFFLUENT LIMITATIONS GUIDELINES OF U.S. EPA SET ON THE BASIS OF BPCTCA AND BATEA

Subcategory	Pollutant Parameter	BTCTCA kg/kkg product		BATEA kg/kkg product	
		Maximum For Any One Day	Daily Average over 30 days	Maximum For Any One Day	Daily Average over 30 days
Electric Arc Furnace (Wet Air Pollution Control methods)	Suspended Solids	0.0312	0.0104	0.0156	0.0052
	Fluoride			0.0126	0.0042
	Zinc			0.0030	0.0010
	pH	6.0 to 9.0		6.0 to 9.0	
Vacuum Degssing	Suspended Solids	0.0156	0.0052	0.0078	0.0026
	Zinc			0.0015	0.0005
	Manganese			0.0015	0.0005
	Lead			0.00015	0.00005
	Nitrate (as NO_3)			0.0141	0.0047
	pH	6.0 to 9.0		6.0 to 9.0	
Continuous Casting	Suspended Solids	0.0780	0.0260	0.0156	0.0052
	Oil and Grease	0.0234	0.0078	0.0156	0.0052
	pH	6.0 to 9.0		6.0 to 9.0	

*Taken from "Development of Effluent Limitation guidelines and New Source Performance Standards For The Steel Making Segment of the Iron and Steel Manufacturing Point Source Category", EPA-440/1-74-024-1).

APPENDIX B

In connection with the development of information of the current waste-treatment practices of the iron and steel industry, a number of integrated steel mills and water treatment companies were visited. Also a number of environmental engineers and specialists were consulted in this area. Following is a list of the contacts made in connection with this work.

The steel companies and the personnel visited are as follows:

(i) Inland Steel Co.
East Chicago Indiana
Mr. John Brough
Director of Air and Water Control

(ii) Interlake Steel Corp.
Chicago, Illinois
Mr. Fred Krikau
Director, Environmental Control

(iii) U.S. Steel Gary Works
Gary, Indiana
Mr. J. H. Dickerson
Supdt. of Environmental Control

(iv) Armco Steel Corp.
Middletown, Ohio
Mr. Donald R. Perander
Environmental Engineering

(v) Kaiser Steel Corp.
Fontana, California
Mr. R. E. Garner
Asst. to Works Manager

Chemical Companies and Personnel Visited:

(i) Nalco Chemical Co.
Oakbrook, Illinois
Mr. Alex J. Bajusz
Industry Manager for Steel and Primary Metals

(ii) Betz Laboratories
Lansing, Illinois
Mr. Richard Stone
Area Manager for Steel Industry

(iii) Calgon Corp.
Pittsburgh, Pa.
Mr. George Peabody
Market Manager, Water Managment

Mr. L. J. Persinski
Manager, Industrial Water Treatment Research

Other Groups:

(i) Chester Engineers,
Environmental Engineers & Planners
Coraopolis, Pa.
Mr. Walter Zabban
Industrail Waste Consultant

(ii) Hydrotechnic Corp.
New York, NY
Mr. H. J. Kohllman
Vice President,
Engineering Manager

(iii) Prof. George St. Pierre,
Department of Metallurgy
Ohio State University
Columbus, Ohio

(iv) Prof. J. Patterson
Environmental Engineering
Illinois Institute of Technology
Chicago, Illinois

(v) American Iron and Steel Institute
Task Force Committee headed by
Mr. William Benzer at Pittsburgh, Pa.